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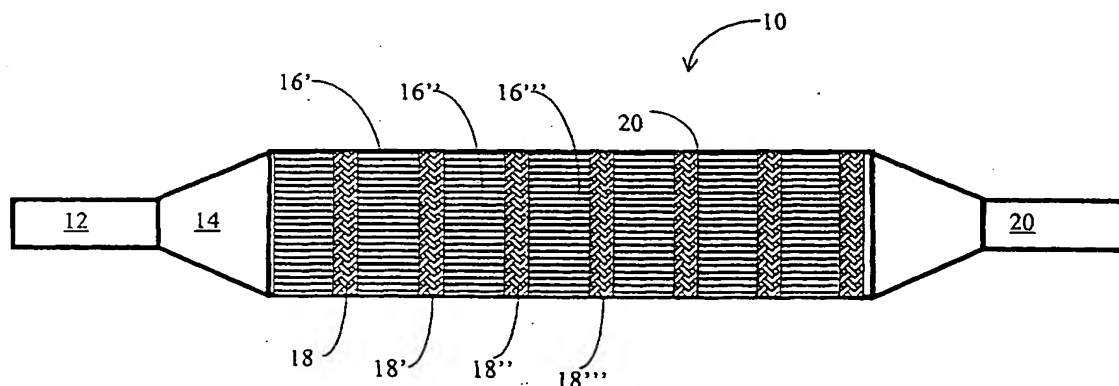
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(54) Title: MULTI-STAGE EXHAUST GAS PURIFIER



(57) Abstract: Diesel or other combustion exhaust is passed through an opening section (14) in the device (10) to direct flow into a treatment zone containing at least one monolith section (16) and one filter screen section (18). Both sections are shown repeated downstream of the opening section (14) of the treatment chamber enclosed by wall structure (15). Following treatment, the exhaust gas is passed from the last of the treatment sections to exit (20). Either one or both of sections (16 and 18) can be catalyzed, either by pretreatment or by use of a fuel borne catalyst, e.g., containing platinum and/or other metal such as cerium or iron.

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MULTI-STAGE EXHAUST GAS PURIFIER

DESCRIPTION

Background Of The Invention

The invention concerns a new device and process for improving purifying internal combustion engine exhaust gas by effectively removing particulate matter (PM) at low cost. The invention provides an economical and effective answer to the problems associated with controlling particulates and permits using effective measures for reducing NO_x without suffering major penalties in fuel consumption, particularly for mobile diesel and other lean-burn engines.

Diesel and lean-burn gasoline engines provide advantages in fuel economy and are favored for this reason. However, when operated for fuel economy and low PM emissions, they produce large quantities of NO_x during normal operation, and there is no known technology that is available to take advantage of their economy without suffering the penalty of NO_x emissions. On the other hand, when primary measures (actions that affect the combustion process itself) are taken to reduce NO_x in lean-burn engines, fuel economy is also usually reduced and PM emissions are increased. This has led to the development of a variety of means to handle PM formed as combustion is conducted under conditions lowering the production of NO_x.

Prominent among these are particulate filters, which encompass a wide variety of forms. They may be particulate or reticulated ceramic foam. They may encompass honeycomb-like structures, often with blocked passageways and small openings between adjacent passageways. Metal mesh filters, pelletized refractory materials such as alumina, and ceramic fibrous mats are all used as diesel particulate filters.

Most current diesel particulate filters (DPF) are single stage devices. There are two primary types: extruded monolith filters and candle filters made from woven or wound fiber. Filters are usually designed for 85% reduction of PM by mass in one stage. Both types have been prone to failure; the failures are caused by excessive buildup of heat and/or pressure resulting in a localized fracture or hole in the filter. The result can be a massive loss in efficiency and effective failure.

Common to all of these structures is the fact that after a reasonably short period of time, they become clogged with the material they are intended to remove. They must be regenerated, either on the vehicle or in a furnace or the like. The soot (PM) builds up on the filter unless it is oxidized.

Catalysts can enhance oxidation. There are several oxidation mechanisms available for use in PM filters. The soot primarily contains carbon and absorbed hydrocarbons. While the hydrocarbons can be quite easily oxidized by oxygen in the presence of catalysts, the elemental carbon is not easily oxidized at the temperatures prevailing in typical diesel engine exhausts.

Carbon can be catalytically oxidized in at least two ways in a typical exhaust gas mixture containing NO_x , excess oxygen and particulates, usually at temperatures over 400°C . In some systems, heat must be added to the exhaust to obtain the necessary temperature to initiate combustion of the soot.

In one of the noted two catalytic oxidation mechanisms, the carbon-NO reaction, carbon is selective in reducing NO to N_2 at temperatures of 600°C and above by surface chemistry. It has been shown in engine tests that when platinum and cerium are used as a fuel borne catalyst (FBC), there is substantial reduction of NO_x to N_2 simultaneous with the oxidation of carbon; it has been postulated that the combination of platinum and cerium is catalyzing the selective reduction of NO by carbon. Some of the NO_x reduction

is measured “engine out” but more reduction is measured when a particulate filter is used – consistent with the fact that more residence time is provided in the filter.

In the second of these two catalytic oxidation mechanisms, the carbon-NO₂ reaction, is the reaction in the presence of NO₂. As typically encountered in the field, NO in exhaust is oxidized over a catalyst, typically of platinum, to NO₂. The resulting NO₂ reacts with carbon to form CO or CO₂ and NO (again). See U. S. Patent No. 4,902,487, to Copper, *et al.*, in this regard. They catalytically treat the exhaust to convert NO to NO₂ and there is no reduction of NO_x to N₂.

As note, some systems provide for adding heat to the exhaust to obtain the necessary temperature to initiate combustion of the soot. In one such system, U.S. Patent No. 5,203,166, to Miller describes a diesel engine emissions control system including a particulate filter system and a pair of heaters on catalyzed particulate filters. The heaters operate to regenerate one of the filters while the other is being used.

Also, U.S. Patent No. 5,294,411, to Breuer, *et al.*, describes an electrically-heated catalyst carrier body utilizing rhodium or platinum as the oxidizing catalyst.

In another approach, European Patent Application No. 743 429 describes a diesel exhaust particulate filter that includes an oxidation catalyst. Diesel fuel is introduced upstream of the oxidation catalyst to raise the temperature of the exhaust gas to heat the catalyst to burn away the PM.

Many other patents describe variations on catalytic devices and systems for oxidizing PM. Among them, European Patent Application No. 764 455 describes a sintered fiber web as the device for removing PM from the exhaust gas. The web may be treated to form an alumina film on the surface of the fibers and optionally a catalyst may be placed on those alumina-coated fibers.

In U.S. Patent No. 4,510,265, Hartwig, describes a diesel engine exhaust gas catalyzed filter which is said to be self-cleaning and employs an oxidation catalyst of a combination of platinum and silver vanadate material. The example shows removal of accumulated carbon by placement of the filter in a furnace variously at temperatures of just greater than 475° C for 20% burn off to just over 600° C for 80% burn off.

U.S. Patent No. 4,711,870, to Yamada, *et al.*, also shows a porous ceramic body used to oxidize diesel soot. The active catalyst is said to be one comprising: (a) copper or a copper compound; (b) vanadium or a vanadium compound; (c) zirconium, aluminum, nickel, iron, manganese, lanthanum, chromium, zinc, lead or cerium, or a compound thereof; and optionally, (d) platinum, rhodium, or palladium, or a compound thereof. These catalysts are also said to allow the particulate burning temperature to be lowered below that required prior to the date of the Yamada, *et al.*, patent. The temperature for removing 90% of the soot found in a control sample of the catalyzed porous body is shown in Example 12 to be in the neighborhood of 460° to 470° C. The conversion of sulfur dioxide to sulfur trioxide was shown to be typically between 15 and 33%.

Also, U.S. Patent No. 4,759,918, to Homeier, *et al.*, shows a Platinum Group metal (platinum, palladium, or rhodium) as a catalytic soot removal device. Example 6 of the patent shows a diesel soot combustion efficiency of 95% at 400° C by use of a platinum catalyst on a titania support.

U.S. Patent No. 5,000,929, to Horiuchi, *et al.*, shows a similar catalyst for diesel soot removal made up of a support, typically of an inorganic refractory oxide, and having palladium and the oxide of at least one of praseodymium, neodymium, and samarium as components.

U.S. Patent No. 5,213,781, to Abe *et al.*, and its division, U.S. Pat. No. 5,340,548, describe a porous diesel engine exhaust filter also catalyzed, *e.g.*, using an alkali metal, a

copper metal, a vanadium element, and at least one rare earth element. The PM is said to be oxidized at 400° C.

U.S. Patent No. 5,330,945, to Beckmeyer, *et al.*, shows a diesel fuel exhaust filter containing a zeolite-based wash coat material. The preferred Y-type zeolite is exchanged with a precious metal to form the active material.

European Patent Application No. 714 652, shows a catalyst for treatment of diesel engine exhaust gas comprising a three-dimensional support structure coated with a platinum and/or a palladium carrying refractory inorganic oxide powder further containing a metal selected from the group consisting of tungsten, antimony, molybdenum, nickel, vanadium, manganese, iron, bismuth, cobalt, zinc, and the alkaline earth metals.

European Patent Application No. 508 513, shows use of a Y-type zeolite supported on a ceramic or a metal monolith. The monolith is used in treating diesel fueled engine exhaust.

European Patent Application No. 160 482, shows a self-cleaning diesel exhaust particulate filter having as its oxidic catalyst mixture, a platinum group metal and an alkaline earth metal. Oxidation temperatures in the neighborhood of 350°C appear to have been achieved using such technology.

European Patent Application No. 600 442, to Nippon Shokuvai Company, utilizes iron as the active catalytic component in a diesel engine exhaust gas purification catalyst.

European Patent Application No. 658 369 utilizes a diesel exhaust trap utilizing an oxidizing catalyst made up of platinum, rhodium, copper or vanadium oxide, composite oxides such as perovskites such as LaMnO_3 and LaCrO_3 , a part of which may be replaced with alkali metals or alkaline earth metals such as strontium, potassium, or

lithium. The examples showed initial oxidation temperatures (for carbon particulates) to be from about 280° to 427° C.

European Patent Application No. 092 023, shows a diesel exhaust trap having an oxidation catalyst of metallic copper or copper compound, metallic molybdenum, metallic vanadium, a molybdenum or vanadium compound, and an alkali metal compound. The catalytic material is preferably placed on a carrier of titania, γ -alumina, or silica-alumina. It is preferably used with a metallic platinum, palladium, or rhodium component for enhanced catalytic activity.

Despite the availability of devices and systems of the type described there remains a current need for an economical and effective answer to the problems associated with reducing particulates for this purpose alone and to permit use of technologies that can reduce NO_x without suffering major penalties in fuel consumption, particularly for mobile diesel and other lean-burn engines.

Summary Of The Invention

The invention provides a new device and a new process addressing the above needs.

A multi-stage filter is made in which each stage is designed for partial reduction of particulate matter (PM) – in some cases only 20 to 50% as opposed to 85% in current single stage filters. For example, a multi-stage filter filtering at 50% efficiency requires four stages to achieve an equivalent overall filtration rate, and a filter with a filtration efficiency of 20% per stage requires nine stages.

It is proposed that a multi-stage filter can be made using segments of monolith “flow through” section alternatively with filtration segments. The monolith can be cordierite, silicon carbide or other material and may be catalyzed during the manufacture

as is done for diesel oxidizers or catalyzed by deposit over time of a fuel borne catalyst (FBC). The filter segments can be of ceramic foam, sintered metal or compressed wire or fiber. Essentially, these filter sections are more open in pore size than single filters and will often be of a deep bed form, not a membrane.

The filter is an assembly of stages with a monolith followed by a filter segment followed by a monolith and so on (as illustrated in the accompanying drawings). The overall efficiency will depend upon the volume available for the components, the number of stages for a particular designed efficiency and the back pressure limit of the system. Monolith sections can be directly abutted to the filter section, but it may be advantageous to provide a gap between sections to allow mixing.

In one specific aspect, the invention provides a method comprising passing combustion gases through a multi-stage treatment zone containing at least one monolith section and one filter screen section within a treatment chamber. Desirably, either one or both of said sections are catalyzed, either by pretreatment or by use of a fuel borne catalyst, *e.g.*, containing platinum or other platinum group metal (PGM), including palladium, rhodium, ruthenium, osmium, and iridium, and/or other metal such as cerium or iron. Also, it is preferred that from 2 to 10 sections of each the monolith and the screen filter are employed.

In another aspect, the invention provides a device comprising a multi-stage treatment zone containing at least one monolith section and one filter screen section within a treatment chamber.

Many of the preferred aspects of the invention are described below. Equivalent structures, procedures and compositions are contemplated.

Description Of The Drawings

The invention will be better understood and its advantages will be more apparent when the following detailed description is read in light of the accompanying drawings, wherein:

Figure 1 is a schematic view of an embodiment of the invention wherein a portion of the exhaust gas, produced by the combustion of diesel fuel is passed through an exhaust purification device in accord with the invention; and

Figure 2 is a schematic view of an embodiment of the invention, showing the exhaust purification device in accord with the invention in greater detail than in Figure 1.

Description Of The Invention

As noted above, the invention relates to a new device and a new process addressing the above needs and is intended for use with combustors such as turbines, boilers, furnaces, process heaters, heat recovery units, diesel engines, spark ignition engines and the like, utilizing carbonaceous, *e.g.*, fossil or bio-derived, fuels such as distillates, residual and gaseous fuels and various fatty acid esters and like fuels.

Also, as noted above, oxidation can be by oxygen at temperatures over 400° C. Catalysts are required to promote oxidation. For oxidization below 400° C, the oxidation reaction mechanism is at least partially the carbon-NO₂ reaction, and the reaction proceeds much more slowly than oxidation at higher temperatures. At the lower temperatures, longer residence time of the soot particle (*i.e.*, carbon, PM) on the catalytic surface is required. Catalytic activity results from the catalyst on the surface upon which the particle resides and upon catalyst "tightly bound" in the soot particle.

The invention provides a multi-stage filter that will enhance both the oxidation of carbon and the reduction of NO_x, and will do so with high reliability. We postulate

several possible explanations for these improvements. First, each stage includes a catalyzed monolith section (catalyzed by FBC or precatalyzed) to increase NO_2 concentration before each filter section. The reacted NO_2 is reduced back to NO after the reaction with carbon, but can be reoxidized to NO_2 at the next stage – thus, using the NO more than once and maximizing the effect of the carbon- NO_2 reaction. Second, each stage provides residence time for the soot particles as they progress through the device; and the particles will tend to impinge on the surfaces where they can react with NO or NO_2 and agglomeration is promoted. Larger agglomerations become easier to filter in subsequent stages. Next, we believe that increased residence time, while promoting reaction under the carbon-NO reaction, *e.g.*, catalyzed by a fuel borne catalyst (FBC) comprising platinum and cerium, also results in enhanced NO_x reduction. The soot particle is effectively reacting under this carbon-NO reaction whenever and wherever it touches a surface in the monolith or filter segments. Finally, filter segments may be varied in porosity through the assembly. For optimum efficiency it may be desirable to have the first stages more open in pore size than the latter stages.

Figure 1 is a schematic view of an embodiment of the invention wherein a portion of the exhaust gas, produced by the combustion of diesel fuel is passed through an exhaust purification device 10 in accord with the invention. Figure 1 shows a passage 12 for receiving exhaust from the engine. The exhaust is passed through an opening section 14 in the device 10 to direct flow into a treatment zone containing at least one monolith section 16 and one screen filter section 18. Both sections are shown repeated as 16', *etc.*, and 18', *etc.*, respectively, downstream of opening section 14 of treatment chamber enclosed by wall structure 15. Following treatment, the exhaust gas is passed from the last of the treatment sections to exit 20. Figure 2 is a schematic view of an embodiment of the invention, showing the exhaust purification device in accord with the invention in greater detail than in Figure 1.

In the Figures, section 16 comprises a monolith of the type typically employed for pass through oxidation catalysts. It will preferably be of a suitable ceramic or other core

material in a simple honeycomb or other configuration with passages substantially continuously extending through the horizontal extent of the device. If desired, undulations or other discontinuities can be formed into the individual channels extending through the section 16.

The materials used in the monolith stages 16, 16', *etc.*, can be the same from stage to stage (for multi-stage devices) or could vary between stages, using one or more of extruded sections and metal assemblies or very open foam or sintered materials. The monolith is easily made and readily available.

It is within the scope of the invention that the monolith sections 16, 16', *etc.*, and the filter or screen filter members 18, 18', *etc.*, may be of similar or the same construction with one another in devices having more than one stage of each, and that more or less screen members may be used. The monolith sections and screen sections can be employed as pairs in any number of stages, *e.g.*, from 2 to 10, say 3 to 6, or can be in unequal number together with other functional components where desired.

Materials of construction for the screen sections, for example be porous ceramics, porous carbon, porous metal, ceramic foam, carbon foam, and metal foam, sintered metal, ceramic and high temperature fibers, may be used to form screen filter structure 18, either used alone, or in combination with one or more screen members 18', 18'', *etc.* As another example, fine mesh screens may be formed from expanded metal or of a woven mesh material, such as compressed wire, compressed wire mesh, felted wire or the like. Preferably, screen structure 18 is formed from a corrosion-resistant material that will not impair the operation of the purification module 18 and devices with which the membrane module is used. Examples of suitable materials for metallic screen members include stainless steels, titanium and alloys thereof, zirconium and alloys thereof, corrosion-resistant alloys, including Inconel® alloys, such as 800H®, and Hastelloy® alloys, and alloys of nickel, such as Monel® metal.

An example of an expanded metal screen member is shown in Figure 2 and generally indicated at 118. Expanded metal sheets include a latticework of metal that defines a plurality of apertures through which exhaust gas may flow. Although other processes may be used, expanded metal sheets may be formed from scoring a sheet of metal and then stretching the metal to provide apertures, such as apertures at the scores. It should be understood that the expanded metal screen member has been schematically illustrated in Figure 2, and that the actual shape of the apertures may vary and will often have shapes that generally appear as geometric or regular shapes. The sheet may also include a solid perimeter region, which may extend all the way around the screen member.

As required by a particular process or combustor, a fuel can be one or a blend of fuels selected from the group consisting of distillate fuels, including diesel fuel, *e.g.*, No. 2 Diesel fuel, gasoline, jet fuel, *e.g.*, Jet A, or the like, and biologically-derived fuels, such as those comprising a "mono-alkyl ester-based oxygenated fuel", *i.e.*, fatty acid esters, preferably methyl esters of fatty acids derived from triglycerides, *e.g.*, soybean oil, Canola oil and/or tallow. Other hydrocarbons, including liquids and gases, *e.g.*, natural gas, or fuels derived from gas and/or emulsion components can be employed.

Cerium and/or iron catalyst levels can be at levels as low as 0.05 ppm and platinum levels can be as low as 0.0005 ppm. A regimen of treatment will utilize effective levels within effective ranges for a time and under conditions, which will achieve one or more of the noted improvements.

The process of the invention can employ as an FBC for catalyzing one or more stages, a fuel-soluble, multi-metal catalyst, preferably comprising fuel-soluble platinum (or other PGM) and either cerium or iron. The cerium and/or iron are typically employed at concentrations of from 0.5 to 20 ppm and the platinum from 0.0005 to 2 ppm, with preferred levels of cerium or iron being from 5 to 10 ppm, *e.g.*, 7.5 ppm, and the PGM being employed at a level of from 0.05 to 0.5ppm, *e.g.*, 0.15 ppm. A preferred ratio of

cerium and/or iron to PGM is from 75: 1 to 10:1. One narrower range is from 60:1 to 15:1.

The fuel can contain detergent (*e.g.*, 50-300 ppm), lubricity additive (*e.g.*, 25 to about 500 ppm), other additives, and suitable fuel-soluble catalyst metal compositions, *e.g.*, 0.1 – 2 ppm fuel soluble platinum group metal composition, *e.g.*, platinum COD or platinum acetylacetonate and/or 2-20 ppm fuel soluble cerium or iron composition, *e.g.*, cerium, cerium octoate, ferrocene, iron oleate, iron octoate and the like. The fuel as defined, is combusted without the specific need for other treatment devices although they can be used especially for higher levels of control on diesels.

A combination of PGM with either iron and/or cerium at low concentrations in fuels is as effective as much higher concentrations of cerium, iron or other metals without platinum in reducing carbon or soot deposits or emissions. Concentrations of a few ppm metals in combination are as effective as 30-100 ppm of iron and/or cerium used alone. These traditional levels of cerium and/or iron are high enough to be factors in causing fouling of heat transfer surfaces due to the high ash burden associated with high metal concentrations in the fuel.

These bimetallic and trimetallic platinum combinations are compatible with standard additive components for distillate and residual fuels such as pour point reducers, antioxidant, corrosion inhibitors and the like.

The catalyst component will preferably comprise a multi-metal fuel soluble catalyst comprised of fuel-soluble platinum (or other PGM) and/or cerium and/or iron. The cerium and/or iron are typically employed at concentrations of from 0.5 to 25 ppm and the platinum from 0.0005 to 2 ppm, with preferred levels of cerium or iron being from 5 to 10 ppm, *e.g.*, 7.5 ppm, and the platinum being employed at a level of from 0.05 to 0.5ppm, *e.g.*, 0.15 ppm. A preferred ratio of cerium and/or iron to PGM is from 75:1 to 10:1.

Among the specific cerium compounds are: cerium III acetylacetonate, cerium III naphthenate, and cerium octoate, cerium oleate and other soaps such as stearate, neodecanoate, and octoate (2-ethylhexoate). Many of the cerium compounds are trivalent compounds meeting the formula: $\text{Ce}(\text{OOCR})_3$ wherein R=hydrocarbon, preferably C_2 to C_{22} , and including aliphatic, alicyclic, aryl and alkylaryl. The cerium is preferred at concentrations of 1 to 15 ppm cerium w/v of fuel. Preferably, the cerium is supplied as cerium hydroxy oleate propionate complex (40% cerium by weight). Preferred levels are toward the lower end of this range.

Among the specific iron compounds are: ferrocene, ferric and ferrous acetylacetonates, iron soaps like octoate and stearate (commercially available as Fe(III) compounds, usually), iron pentacarbonyl $\text{Fe}(\text{CO})_5$, iron naphthenate, and iron tallate.

Any of the platinum group metal compositions, e.g., 1,5-cyclooctadiene platinum diphenyl (platinum COD), described in U.S. Pat. No. 4,891,050 to Bowers, et al., U.S. Pat. No. 5,034,020 to Epperly, et al., and U.S. Pat. No. 5,266,093 to Peter-Hoblyn, et al., can be employed as the platinum source. Other suitable platinum group metal catalyst compositions include commercially-available or easily-synthesized platinum group metal acetylacetonates, platinum group metal dibenzylidene acetonates, and fatty acid soaps of tetramine platinum metal complexes, e.g., tetramine platinum oleate. The platinum is preferred at concentrations of 0.05 – 2.0 ppm platinum w/v (mg per liter) of fuel, e.g., up to about 1.0 ppm. Preferred levels are toward the lower end of this range, e.g., 0.15 – 0.5 ppm. Platinum COD is the preferred form of platinum for addition to the fuel. The cerium or iron are typically employed at concentrations to provide from 0.5 to 25 ppm of the metal and the platinum from 0.0005 to 2 ppm, with preferred levels of cerium or iron being from 5 to 10 ppm, e.g., 7.5 ppm, and the platinum being employed at a level of from 0.1 to 0.5 ppm, e.g., 0.15 ppm. A preferred ratio of cerium and/or iron to platinum is from 75:1 to 10:1.

The combustion according to the invention can be of an emulsion with water, wherein an oil phase is emulsified with water, the water comprising from 1 to 30% water based on the weight of the distillate fuel, residual fuel, aviation kerosene or the like. In the preferred forms, the emulsion will be predominantly of the water-in-oil type and will preferably contain surfactants, lubricity additives and/or corrosion inhibitors in addition to the other components mentioned above. A discussion of suitable emulsion forms and additives is found in U. S. Patent No. 5,743,922. Combustion additives can improve combustion efficiency and reduce particulates without the use of oxidation catalysts or particulate filters for enhanced emissions control on diesel engines. Also, better carbon burn out in open flame combustion sources will lead to lower carbon deposits on heat transfer surfaces and lower soot oxidation temperatures on downstream heat recovery devices.

The above description is intended to enable the person skilled in the art to practice the invention. It is not intended to detail all of the possible modifications and variations which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such modifications and variations be included within the scope of the invention which is seen in the above description and otherwise defined by the following claims. The claims are meant to cover the indicated elements and steps in any arrangement or sequence which is effective to meet the objectives intended for the invention, unless the context specifically indicates the contrary.

CLAIMS

1. A method for reducing the particulate content of combustion exhaust:
comprising passing combustion gases through a multi-stage treatment zone containing at least one monolith section and one filter screen section within a treatment chamber.
2. A process according to claim 1 wherein either one or both of said sections are catalyzed, either by pretreatment or by use of a fuel borne catalyst containing a platinum group metal and/or cerium and/or iron.
3. A process according to claim 1 wherein from 2 to 10 sections of each the monolith and the screen filter are employed.
4. A particulate removal device comprising:
a multi-stage treatment zone containing at least one monolith section and one filter screen section within a treatment chamber.
5. A process according to any of claims 1 to 4 wherein NO_x is reduced simultaneously as part of the process of oxidation of carbon from particulates.
6. A process according to any of claims 1 to 5 wherein the platinum group metal compound comprises a composition selected from the group consisting of 1,5-cyclooctadiene platinum diphenyl, platinum group metal acetylacetonates, platinum group metal dibenzylidene acetonates, and fatty acid soaps of tetramine platinum metal complexes.
7. A process according to any of claims 1 to 6 wherein the a metal compound in addition to a platinum group metal compound is employed and comprises a composition selected from the group consisting of cerium III acetylacetonate, cerium III naphthenate,

and cerium octoate, cerium oleate and other soaps such as stearate, neodecanoate, and octoate (2-ethylhexoate), ferrocene, ferric and ferrous acetylacetonates, iron soaps like octoate and stearate, iron pentacarbonyl $\text{Fe}(\text{CO})_5$, iron naphthenate, and iron tallate.

8. A process according to any of claims 1 to 7 wherein platinum is employed at concentrations of 0.05 – 2.0 ppm platinum w/v (mg per liter) of fuel.
9. A process according to any of claims 1 to 8 wherein cerium and/or iron are employed at concentrations to provide from 0.5 to 25 ppm of the metal and the platinum from 0.0005 to 2 ppm.
10. A process according to any of claims 1 to 9 wherein cerium and/or iron are employed at concentrations to provide from 0.5 to 25 ppm of the metal and platinum, is employed at a level of from 0.1 to 0.5ppm.
11. A process according to any of claims 1 to 9 wherein cerium and/or iron is employed at ratio to platinum of from 75:1 to 10:1.

and cerium octoate, cerium oleate and other soaps such as stearate, neodecanoate, and octoate (2-ethylhexoate), ferrocene, ferric and ferrous acetylacetonates, iron soaps like octoate and stearate, iron pentacarbonyl $\text{Fe}(\text{CO})_5$, iron naphthenate, and iron tallate.

8. A process according to any of claims 1 to 7 wherein platinum is employed at concentrations of 0.05 – 2.0 ppm platinum w/v (mg per liter) of fuel.
9. A process according to any of claims 1 to 8 wherein cerium and/or iron are employed at concentrations to provide from 0.5 to 25 ppm of the metal and the platinum from 0.0005 to 2 ppm.
10. A process according to any of claims 1 to 9 wherein cerium and/or iron are employed at concentrations to provide from 0.5 to 25 ppm of the metal and platinum, is employed at a level of from 0.1 to 0.5 ppm.
11. A process according to any of claims 1 to 9 wherein cerium and/or iron is employed at ratio to platinum of from 75:1 to 10:1.
12. A multi-stage filter that will enhance both the oxidation of carbon and the reduction of NO_x , comprising a plurality of stages wherein at least two stages include:
a filter section and a catalyzed monolith section to increase NO_2 concentration before each filter section.

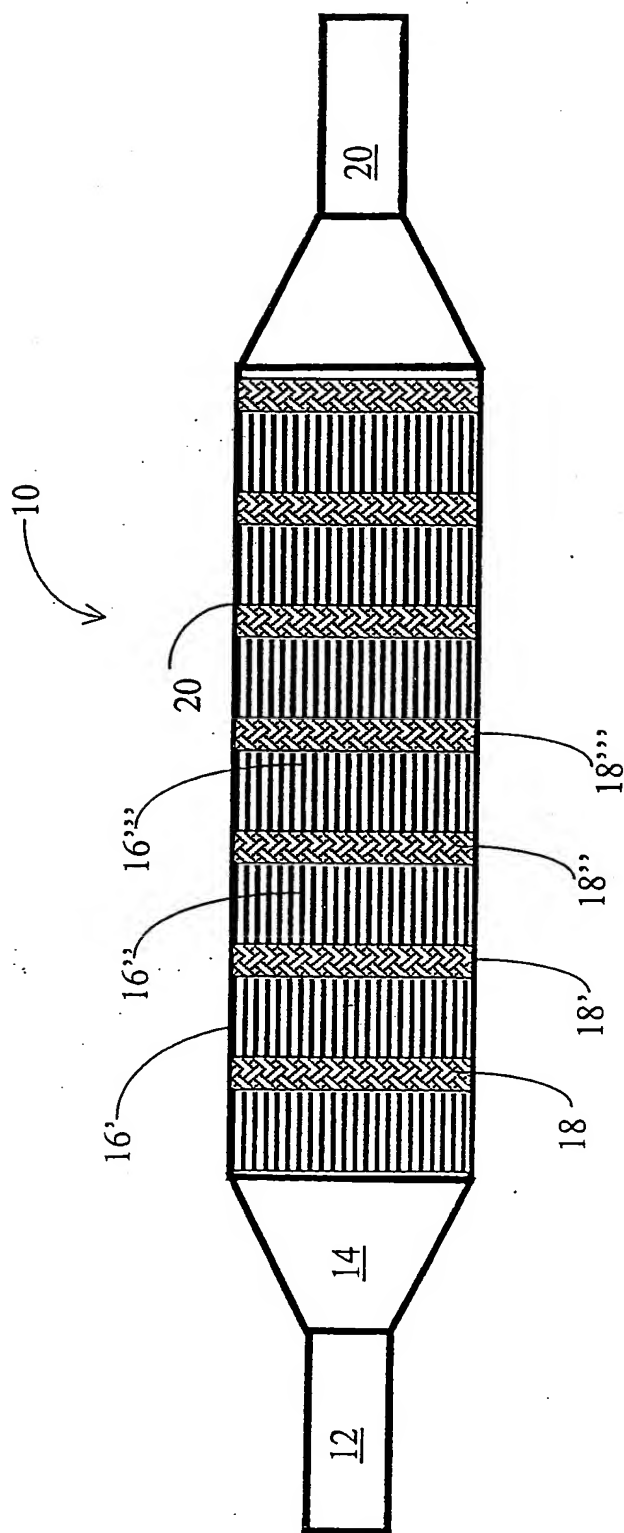


Figure 1

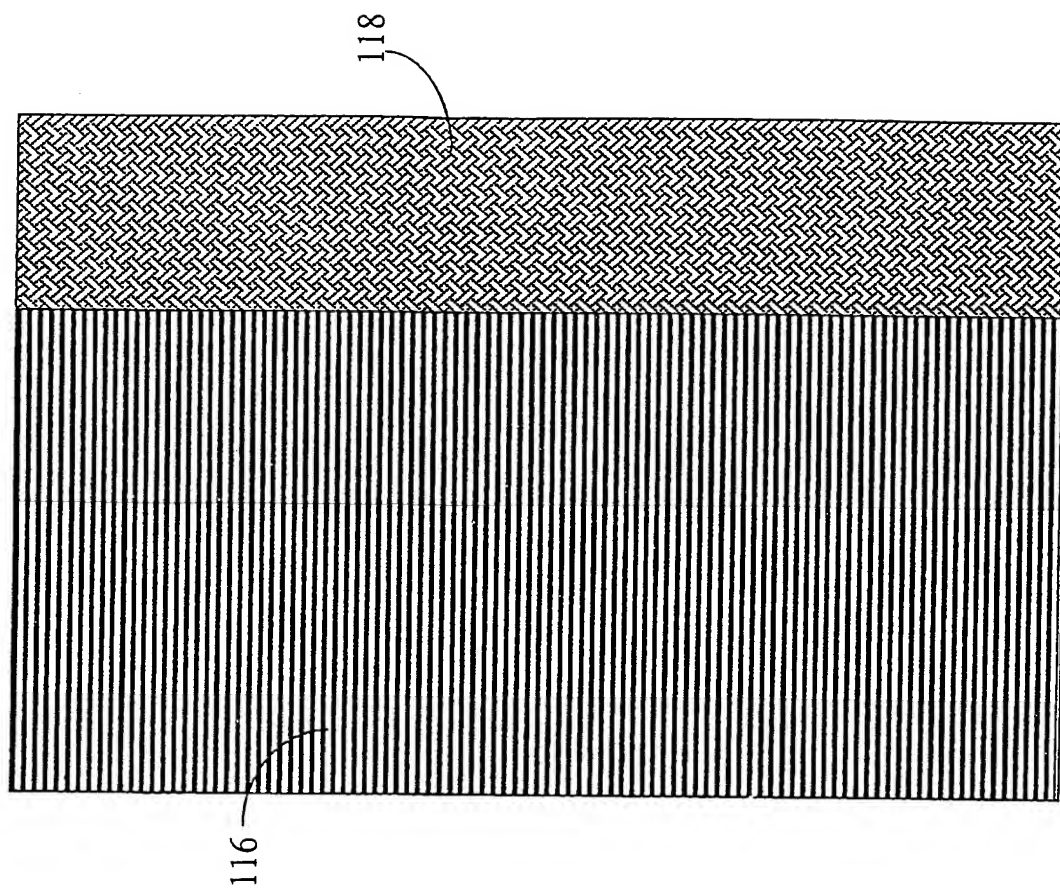


Figure 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/03796

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01D 50/00, 53/56; B01J 35/04
US CL : 422/171, 177, 180; 423/215.5, 235, 239.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 422/170, 171, 177, 180; 423/210, 215.5, 235, 239.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 5,318,755 A (KUIVALAINEN et al) 07 June 1994, see entire document.	1, 3-4, 12 — 2, 5-11
X — Y	US 4,902,487 A (COOPER et al) 20 February 1990, see entire document.	1-5, 12 — 6-11
X — Y	US 4,416,674 A (McMAHON et al) 22 November 1983, see entire document.	1, 3, 12 — 2, 4-11
X — Y	US 4,072,471 A (MORGAN, JR. et al) 07 February 1978, see entire document.	1, 3-4, 12 — 2, 5-11

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

30 April 2003 (30.04.2003)

Date of mailing of the international search report

19 MAY 2003

Name and mailing address of the ISA/US

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INTERNATIONAL SEARCH REPORT

PCT/US03/03796

Continuation of B. FIELDS SEARCHED Item 3:

East

Search terms: multi-stage, NOx, particulate, monolith, filter